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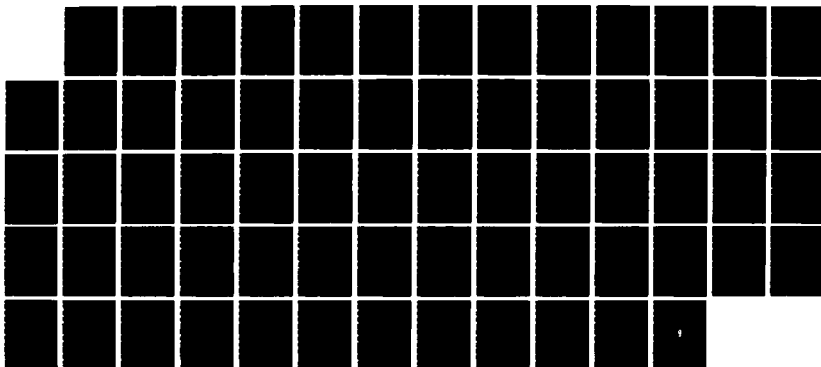
QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF  
CATIONIC POLYMERIZATION (U) JOHNS HOPKINS UNIV BALTIMORE  
ND J J KAUFMAN 15 MAR 86 N00014-80-C-0003

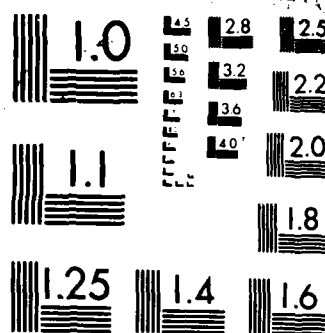
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

- 1. Conversion of Additional Programs to CRAY Vector Supercomputers and Program Enhancements
- 2. MRD-CI Calculations for the Propagation Step in Cationic Polymerization of Energetic Oxetanes
- 3. NMR Spectra of Oxetanes
- 4. Ab-Initio Atom-Class - Atom-Class Potential Functions and Independent Confirmations of the Validity of Our Ab-Initio MODPOT/VRDDO Energy Partitioned Method For Intermolecular Interactions.

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→ 8. Geometry Optimizations at the MC-SCF/CI Level  
 ✓ POLY-CRYST

I. This past year we enlarged for the CRAY XMP (COS and CTSS) the MRD-CI program to include more active orbitals, more reference configurations, more roots and larger basis sets. An MRD-CI population analysis program was written. A program was written to locate centroids of localized molecular orbitals. We implemented and initiated prototype calculations on a major program system GAMESS which has the capability of optimizing molecular geometries by a derivative method at the SCF, MC-SCF/CI and CASSCF levels.

II. We developed and implemented a new approach based on localized occupied and virtual orbitals in the interaction region with the remainder of the localized molecular orbitals being folded into an effective CI-Hamiltonian. This method is completely general and applicable to reactions and molecular decompositions of energetic compounds for ground and electronically excited states.

We initiated a major research effort on ab-initio MRD-CI calculations on opening the ring of oxetane or protonated oxetane and on the opening of the protonated oxetane ring in the course of interaction with oxetane.

We have carried out MRD-CI calculations for a great many geometries for various paths of attack for the system oxetane plus protonated oxetane. We have varied the angle of opening of the protonated oxetane ring (ring 'A'), varied the internuclear distance between the rings and the angle between the plane of the oxetane (ring 'B') and the plane of the protonated oxetane ring. (keywords: *could*)

III. The <sup>17</sup>O NMR spectra of several oxetanes were examined experimentally by Walter S. Koski to see if they could be used to calibrate our computed electrostatic molecular potential contour (EMPC) maps for the basicity of oxetane and its derivatives.

IV. We recently had the opportunity to validate the reliability both of the SCF intermolecular interaction calculations using our ab-initio MODPOT basis set and of the semi-theoretical expressions we had been using for dispersion energy by comparing our results on the nitromethane dimer with those of recent larger basis set [4,3,1/2,1] all-electron calculations on the nitromethane dimer, [SCF, SCF/SDQ-MBPT(4), SCF/dispersion energy  $E_{disp}^{(200)}$ ].

Our results further suggest that it appears feasible to correct for the small differences in the absolute intermolecular interaction energies between the ab-initio MODPOT SCF results and those of all-electron larger basis set SCF calculations by the difference in the  $E_{EL,MTP}^{(1)}$  calculations with the different basis sets. In addition, the semi-theoretical method we have been using to estimate dispersion energies proved to give values very close to  $E_{DISP}^{(200)}$  (variation-perturbation) that had been calculated using a larger all-electron basis set.

V. We explored a number of features of the GAMESS program which has the capability of optimizing geometries by a derivative method at the MC-SCF and CASSCF levels as well as at the SCF level. We are exploring and using more of the new options in the GAMESS program for our studies on the energetic oxetanes.

VI. Commensurate with the ONR priorities expressed to us by our ONR Contract Monitor to devote our major attention to the problem of the cationic polymerization of oxetanes, we only devoted very minimal effort to further development and testing of the POLY-CRYST program (for ab-initio calculations of crystals and polymers).

For efficiency we initiated changes in the way the integrals are picked up. We also ran a few test calculations.

Report Number ONR-NR093964-TR7

SUMMARY

ANNUAL REPORT

QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF CATIONIC  
POLYMERIZATION

and

THEORETICAL PREDICTION OF CRYSTAL DENSITIES

and

DECOMPOSITION PATHWAYS OF ENERGETIC MOLECULES

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The Johns Hopkins University  
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Joyce J. Kaufman, Principal Investigator  
Department of Chemistry  
The Johns Hopkins University

CONCISE SUMMARY

I. Conversion of Additional Programs to CRAY Vector Supercomputers and Program Enhancements

Our exploratory ab-initio MRD-CI (multireference double excitation-configuration interaction) calculations on the reaction of oxetane with protonated oxetane for the propagation step in cationic polymerization indicated that even for oxetane and certainly for the substituted oxetanes we were going to have to consider more active orbitals, more reference configurations, more roots and larger basis sets than the MRD-CI program was capable of handling at that time.

Thus, this past year we enlarged these aspects of the MRD-CI program for the CRAY XMP Computers (for both the COS and CTSS operating systems).

A population analysis program to calculate charges on the atoms and total overlap populations between atoms from the density matrix following the final CI calculations was also written.

To help in choosing molecular orbitals most optimally localized in the reaction (bond making and bond breaking) region, we wrote a program to locate the centroids of each localized molecular orbital.

This past year we implemented and initiated prototype calculations on a major program system GAMESS (Gaussian Atomic and Molecular Energy Systems) which has the capability of optimizing geometries by a derivative method not only at the SCF level but also at the MC-SCF/CI (multi-configuration SCF/configuration interaction) or CASSCF (Complete Active Space MC-SCF) levels. This can prove important in any calculations on energetic compounds involving nitro, nitrate and nitramino groups.

As a result of our expertise on CRAY computers, we acted as "friendly users" on the NSF CRAY XMP-48 supercomputer at the San Diego Supercomputer Center (SDSC) located at GTA San Diego, California for December 1985 prior to the official opening of that center.

As a result of our interaction with that SDSC computer center, by invitation we have been serving on their review committee for granting NSF computer time on their CRAY XMP-48.

## II. MRD-CI Calculations for the Propagation Step in Cationic Polymerization of Energetic Oxetanes

Our major research this past year has been on theoretical quantum chemical ab-initio MRD-CI (multireference double excitation - configuration interaction) calculations on the mechanism of the propagation step of cationic polymerization of oxetane by protonated oxetanes. The oxetane - protonated oxetane systems (especially the substituted ones) are larger than any molecular reacting systems for which any MRD-CI calculations have been carried out. We developed and implemented a new approach based on localized occupied and virtual orbitals in the interaction region with the remainder of the localized molecular orbitals being folded into an effective CI Hamiltonian. This method is completely general and applicable to reactions and molecular decompositions of energetic compounds for ground and electronically excited states.

This past year we initiated a major research effort on ab-initio MRD-CI calculations on opening the ring of oxetane or protonated oxetane and on the opening of the protonated oxetane ring in the course of interaction with oxetane. We considered the following localized orbitals explicitly in the MRD-CI calculations: in protonated oxetane 'A' ring  $C_{4A}-O_{1A}$ ,  $C_{2A}-O_{1A}$ , the lone pair on  $O_{1A}$ ,  $O_{1A}-H^+$ , and the bonds connecting hydrogens to  $C_{2A}$  and  $C_{4A}$ , in oxetane 'B' ring,  $O_{1B}-C_{2B}$ ,  $O_{1B}-C_{4B}$ , the lone pair on  $O_{1B}$  and inter-ring  $O_{1B}-C_{4A}$ .

We have carried out MRD-CI calculations for a great many geometries for various paths of attack for the system oxetane plus protonated oxetane. We have varied the angle of opening of the protonated oxetane ring (ring 'A'), varied the internuclear distance between the rings and the angle between the plane of the oxetane ring (ring 'B') and the plane of the protonated oxetane ring.

The most favorable pathway we have found is for  $O_{1B}$  to attack linearly along the  $C_{4A}-O_{1A}$  bond direction in an  $S_N2$  type of attack with at least a partial inversion of the H atoms on  $C_{4A}$  with concomitant opening of the  $C_{4A}-C_{1A}$  bond.

## III. $^{17}O$ NMR Spectra of Oxetanes

The  $^{17}O$  NMR spectra of several oxetanes were examined experimentally by Walter S. Koski to see if they could be used to calibrate our computed electrostatic molecular potential contour (EMPC) maps for the basicity of oxetane and its derivatives. The results for oxetane and BAMO show that  $^{17}O$  NMR chemical shifts cannot be used directly to make such calibrations. The reasons for this is that two opposing effects contribute to the resultant chemical shift. One is a diamagnetic effect, related to the electron density on the O nucleus, and a second is a paramagnetic effect, due to the



presence of low lying excited states. It is difficult to unscramble these two contributions and get a direct measure of the electron population on the oxygen atom. The sign of the paramagnetic term is opposite to that of the diamagnetic effect. The effects of these two terms are difficult to disentangle quantitatively.

However, a detailed  $^{17}\text{O}$  and  $^{13}\text{C}$  NMR study of substituted oxetanes coupled with other chemico-physical/physicochemical measurements would give us a great deal of insight into the electronic properties of the series of energetic oxetane derivatives of interest to this ONR program.

#### IV. Ab-initio Atom-Class - Atom-Class Potential Functions and Independent Confirmations of the Validity of Our Ab-Initio MODPOT/VRDDO Energy Partitioned Method For Intermolecular Interactions.

We recently had the opportunity to validate the reliability both of the SCF intermolecular interaction calculations using our ab-initio MODPOT basis set and of the semi-theoretical expressions we had been using for dispersion energy by comparing our results on the nitromethane dimer with those of recent larger basis set  $[4,3,1/2,1]$  all-electron calculations on the nitromethane dimer,  $[\text{SCF}, \text{SCF}/\text{SDQ-MBPT}(4), \text{SCF}/\text{dispersion energy } E_{\text{disp}}^{(200)}]$ .

Our results further suggest that it appears feasible to correct for the small differences in the absolute intermolecular interaction energies between the ab-initio MODPOT SCF results and those of all-electron larger basis set SCF calculations by the difference in the  $E_{\text{EL,MTP}}^{(1)}$  calculations with the different basis sets.

In addition, the semi-theoretical method we have been using to estimate dispersion energies proved to give values very close to  $E_{\text{DISP}}^{(200)}$  (variation-perturbation) that had been calculated using a larger all-electron basis set.

We also calculated the  $E_{\text{EL,MTP}}^{(1)\text{SDQ-MBPT}(4)}$  from correlated monomer multipoles using the larger all-electron basis set. These results suggest how one might use  $E_{\text{EL,MTP}}^{(1)\text{SDQ-MBPT}(4)}$  and  $E_{\text{EL,MTP}}^{(1)\text{SCF}}$  results to separate intra and intermolecular contributions to the correlation energy.

#### V. Geometry Optimizations at the MC-SCF/CI Level

We explored a number of the features of the GAMESS program which has the capability of optimizing geometries by a derivative method at the MC-SCF and CASSCF levels as well as at the SCF level. We are exploring and using more of the new options in the GAMESS program for our studies on the energetic oxetanes.

## VI. POLY-CRYST

Commensurate with the ONR priorities expressed to us by our ONR Contract Monitor to devote our major attention to the problem of the cationic polymerization of oxetanes, we only devoted very minimal effort to further development and testing of the POLY-CRYST program (for ab-initio calculations of crystals and polymers).

For efficiency we initiated changes in the way the integrals are picked up. We also ran a few test calculations.

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Department of Chemistry  
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I. Conversion of Additional Programs to CRAY Vector Supercomputers and Program Enhancements

Our exploratory ab-initio MRD-CI (multireference double excitation-configuration interaction) calculations on the reaction of oxetane with protonated oxetane for the propagation step in cationic polymerization indicated that even for oxetane and certainly for the substituted oxetanes we were going to have to consider more active orbitals, more reference configurations and larger basis sets than the MRD-CI program was capable of handling at that time.

Thus, this past year we enlarged these aspects of the MRD-CI program plus adding the capability of taking more roots of the CI matrix. The programs are large and complicated and such changes are not trivial. We also increased the capability for taking more roots in the explicit solving of the CI matrix. This is important if there are potential energy surfaces involving excited states. We first enlarged these aspects of the MRD-CI program on the NRL CRAY XMP-12 which runs under the COS operating system. Because each such MRD-CI calculation on the larger substituted energetic oxetanes can take significant amounts of computer time and a number of different geometries must be calculated for each pair of partners, we also then added these expanded capabilities to the CTSS versions of the MRD-CI program which run on the other CRAY computers.

A population analysis program to calculate charges on the atoms and total overlap populations between atoms from the density matrix following the final CI calculations was also written. This will give important insight into such questions as the relative charges on the  $C_2$  atom in various substituted oxetanes undergoing reaction and the incipient making and breaking of bonds.

To help in choosing molecular orbitals most optimally localized in the reaction (bond making and bond breaking) region, we wrote a program to locate the centroids of each localized molecular orbital. We further extended this strategy by supplementing the choice of localized molecular orbitals with suitable lone pairs or empty orbitals which could take part in making or breaking bonds.

This past year we implemented and initiated prototype calculations on a major program system GAMESS (Gaussian Atomic and Molecular Energy Systems) which has the capability of optimizing geometries by a derivative method not only at the SCF level but also at the MC-SCF/CI (multi-configuration SCF/configuration interaction) or CASSCF (Complete Active Space MC-SCF)

levels. This can prove important in any calculations on energetic compounds involving nitro, nitrate and nitramino groups. The GAMESS program was originally written by Dr. Michel Dupuis of the old NRC<sup>2</sup> (National Resource for Computational Chemistry). Dr. Kaufman had been a visiting scientist at NRC<sup>2</sup> and had collaborated with Dr. Dupuis in using that program for her original GVB and MC-SCF calculations on nitromethane. With the collaboration of Dr. Victor Saunders, the head of the Atomic and Molecular Theory Group at Daresbury, England, we got the Daresbury CRAY COS version of GAMESS running on the NRL CRAY XMP-12. Significant changes had been made by Daresbury to the original GAMESS program to mesh in their ATMOL SCF and CASSCF (Complete Active Space MC-SCF) with the geometry optimization scheme.

As a result of our expertise on CRAY computers, we acted as "friendly users" on the NSF CRAY XMP-48 supercomputer at the San Diego Supercomputer Center (SDSC) located at GTA San Diego, California for December 1985 prior to the official opening of that center. That CRAY runs under a version of the CTSS operating system.

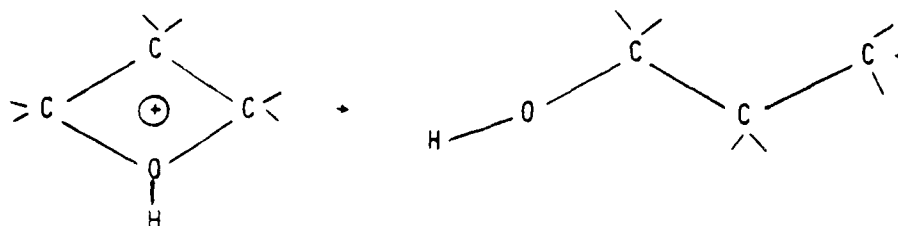
As a result of our interaction with that SDSC computer center, we were asked to serve on their review committee for granting NSF computer time on their CRAY XMP-48. Dr. P. C. Hariharan served at their January 1986 computer allocation committee meeting, Dr. Walter S. Koski served at their March, June, and September meetings and Dr. Joyce J. Kaufman will serve at their December 1986 meeting.

## II. MRD-CI Calculations for the Propagation Step in Cationic Polymerization of Energetic Oxetanes

Our major research this past year has been on theoretical quantum chemical ab-initio MRD-CI (multireference double excitation - configuration interaction) calculations on the mechanism of the propagation step of cationic polymerization of oxetane by protonated oxetanes. Energetic polymers made by cationic polymerization of energetic substituted oxetanes are of significant Navy interest. Our prior theoretical quantum chemical calculations and the electrostatic molecular potential contour (EMPC) maps generated from them, have enabled us to understand the initiation step and to predict the propensity of different energetic substituted oxetanes to undergo cationic polymerization and to pick optimal copolymer partners even prior to synthesis of the monomers themselves. Our current MRD-CI calculations will shed insight on the subsequent propagation step in cationic polymerization and how different copolymer partners would prefer to propagate. This influences the subsequent final polymer.

The oxetane - protonated oxetane systems (especially the substituted ones) are larger than any molecular reacting systems for which any MRD-CI calculations have been carried out. We developed and implemented a new approach based on localized occupied and virtual orbitals in the interaction region with the remainder of the localized molecular orbitals being folded into an effective CI Hamiltonian. This method is completely general and applicable to reactions and molecular decompositions of energetic compounds for ground and electronically excited states.

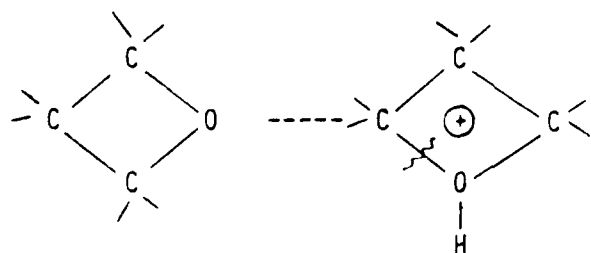
After initiation the succeeding step in cationic polymerization is propagation. In the past some experimentalists had suggested that there would be ring opening of the protonated carbocation



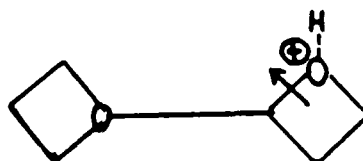
which would then be the propagating species. The experimentalists had further suggested that the more electrophilic a protonated carbocation was, the more efficient a propagating species it would be. Our previous quantum chemical calculations had shown that by any criterion, the protonated carbocation of 3,3-dinitrooxetane would be the best propagating species. Conversely, our EMPC maps had shown that 3,3-dinitrooxetane would have the least propensity to undergo initiation of cationic polymerization. Since 3,3-dinitrooxetane does not undergo cationic polymerization under any usual conditions, it is the initiation step which is dominant in the propensity for cationic polymerization.

However, experimentalists believe that  $1^\circ$  carbocations do not form except under very rare circumstances and are not a very stable species and thus would not be expected to exist long enough in aqueous solution to serve as the propagating species.

Recently (June 1985) several different experimentalists in cationic polymerization suggested to us that a possible mechanism would be attack of protonated oxetanes on oxetanes (or vice versa) with concomitant ring opening of the protonated oxetane according to the following general scheme



Manzer suggested:



Lillya suggested essentially the same overall picture:



Thus we initiated a major research effort on ab-initio MRD-CI calculations on opening the ring of oxetane or protonated oxetane and on the opening of the protonated oxetane ring in the course of interaction with oxetane. MRD-CI calculations are necessary if a bond is being broken or formed since often there are several Slater determinants involved in the electronic wave functions. We have already carried out the ab-initio MRD-CI calculations for a number of different C - O interring distances and angles and different angles of opening of the oxetane and protonated oxetane ring. The substituted oxetanes are large molecular systems and their interactions with protonated substituted oxetanes lead to even larger systems. These are larger molecular systems than have ever been calculated with MRD-CI methods and also exceed the amount of data that can be handled even in the current CRAY-XMP series. Hence, we developed and implemented a new MRD-CI approach based on localized orbitals occupied and virtual in the reaction/interaction region with the remainder of the nonparticipating localized occupied molecular orbitals being folded into an effective CI Hamiltonian.

#### A. Validation of Localized Orbital MRD-CI Technique

Many years ago, we derived and implemented a technique in which the effects of the occupied molecular orbitals from which excitations are not allowed are folded into an effective CI Hamiltonian.<sup>1</sup> This has the advantage that it is no longer necessary to transform the integrals over atomic orbitals to integrals over molecular orbitals from which excitations are not allowed. It is this transformation which is the computer resource (space- and time-wise) intensive part of the MC-SCF or especially of the CI problem.

Use of the effective CI Hamiltonian, employing sets of highest occupied (and lowest unoccupied) conventional delocalized molecular orbitals, is applicable to and has been used previously for calculations of such physical phenomena as ionization potentials, electron affinities and electronic spectra. However, for molecular decompositions and molecular reactions, all of the molecular orbitals in the spatial region of interest will not be among the highest occupied and lowest unoccupied orbitals. Thus, we proposed in 1980,<sup>2</sup> for molecular decompositions and reactions to transform to localized molecular orbitals and to carry out the CI calculations explicitly on the localized molecular orbitals occupied and virtual in the spatial region of interest folding the remainder of the occupied localized molecular orbitals into an effective CI Hamiltonian.<sup>2,3</sup>

We showed by test examples (with a system of such a size that the entire valence space MRD-CI could be run on the NRL CRAY-XMP) that the MRD-CI based on localized orbitals gave a potential energy surface for molecular decomposition essentially parallel to that using the entire valence space MRD-CI. The test example that we chose was the  $\text{H}_3\text{C}-\text{F}$  dissociation of fluoromethane using the full valence space and using only localized orbitals in the dissociation region (folding the remainder of the occupied molecular orbitals into an effective CI Hamiltonian). These calculations were carried out for several purposes:

1. To validate our hypothesis that potential energy surfaces for bond dissociations from MRD-CI calculations based on strictly orthogonal localized molecular orbitals in the bond dissociation region (with the remainder of the occupied orbitals folded into an effective CI Hamiltonian) would be essentially parallel to MRD-CI potential energy surfaces calculated using full valence molecular orbital space. For this purpose we used a standard Dunning contraction of the Huzinaga basis set ( $9^S5^P + 3^S2^P$ ) on C and F and a  $3^S - 1^S$  basis set on the hydrogens and ran MRD-CI calculations allowing excitations from all the occupied valence molecular orbitals.

With this same basis set, we then carried out the MRD-CI calculations using the localized molecular orbitals in the C - F bond and on the F plus the full valence virtual localized molecular orbital space.

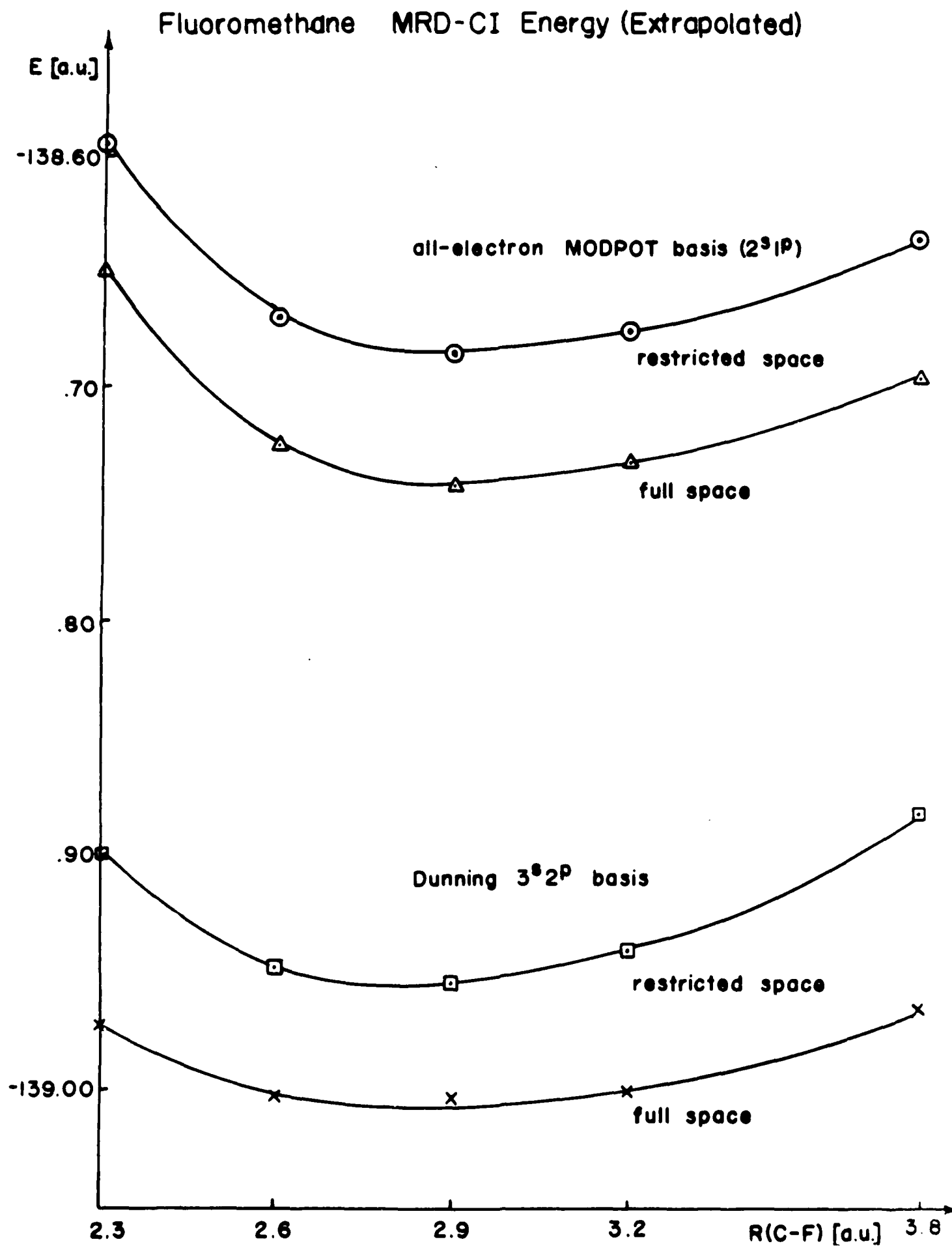
2. To show that MRD-CI potential energy surfaces calculated with the all-electron basis set with the same exponents and contraction coefficients as our customary ab-initio MODPOT valence-electron basis set (incorporating ab-initio effective core model potentials for inner shells) were essentially parallel to those calculated with a more standard Dunning  $9^S5^P + 3^S2^P$  contraction.

The atomic all-electron basis set for this set of MRD-CI calculations was  $10^S6^P + 2^S1^P$  on C and F and the same  $3^S - 1^S$  atomic basis set on H as above. The SCF calculations were carried out and the canonical molecular orbitals were transformed to strictly orthogonal localized molecular orbitals. The MRD-CI calculations were carried out both with the full valence molecular orbital space (occupied and virtual) and then with the localized molecular orbital in the C - F bond plus the full valence virtual orbital space.

The four different potential energy surfaces are shown in Figure 1.



Figure 1.



From Figure 1 it can be seen that:

1. The MRD-CI potential energy surfaces are essentially parallel for the  $9^S5^P + 3^S2^P$  basis set both for the full all-valence electron space and for the restricted localized orbital space.

2. The MRD-CI potential energy surfaces are essentially parallel for the all-electron MODPOT  $10^S6^P - 2^S1^P$  basis set both for the full all valence electron space and for the localized orbital space.

3. The MRD-CI curves are also essentially parallel for the Dunning  $3^S2^P$  and the all-electron MODPOT  $2^S1^P$  basis set.

Thus, the localized orbital MRD-CI approach appears valid and well behaved. This technique holds great promise for calculations on larger systems.

## B. MRD-CI Calculations on the Reaction of Oxetane with Protonated Oxetane.

These MRD-CI calculations for the reaction of protonated oxetane with oxetane are a computationally and labor intensive project. For each different inter- and intra-molecular geometry point, first the SCF calculation must be run, then the resulting SCF canonical delocalized molecular orbitals must be localized. We wrote a program to determine the centroids of the localized bonds compared to the bonds and atoms involved in the interaction/reaction. We found we had to supplement that choice with the empty orbitals and lone pairs that might be involved in the bond making and bond breaking.

Next a small single reference CI calculation must be carried out to determine the major reference configurations. Then a larger MRD-CI calculation is run. The configurations corresponding to all of the single and double excitations are then generated relative to the multireference configuration wave function. The program estimates the energy contribution of each of these single and double excitation configurations by a perturbation procedure. All of the configurations contributing more energy than a predetermined threshold are included explicitly in the CI calculation ( $E_{CI}$ ). Then the energies of the excluded other configurations are added back in by an extrapolation perturbation procedure ( $E_{EXT}$ ) and finally a Davidson type correction is added to correct for size extensivity.

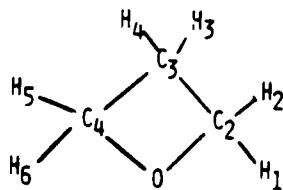
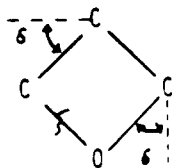
$$E(\text{full CI estimate}) = E(\text{EXT}) + (1 - \sum_p c_p^{\text{ref}})^2 [E(\text{EXT}) - E(\text{Ref})]$$

The MRD-CI method used is that of Buenker and Peyerimhoff and the definitions of the various energies are consistent with those used by them.<sup>4-7</sup>

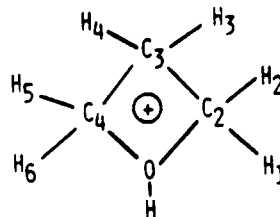
We reported last year that we had carried out test MRD CI calculations on oxetane and protonated oxetane and for their ring opened species using a standard Dunning  $9^5P+3^5P$  all-electron basis set and our ab-initio MODPOT basis set. The MRD-CI results for energy differences showed the same trends for both basis sets. Moreover, the difference in the ab-initio MODPOT MRD-CI energies between (at all oxetane and protonated oxetane (at all CI levels) levels  $E_{CI}$ ,  $E_{EXT}$ ,  $E_{FULL}$ ) was -0.31 a.u. (8.43 ev.) in excellent agreement with the experimental proton affinity of oxetane (8.56 ev.)<sup>8</sup>. The proton affinity contributes sufficient energy to influence the protonated oxetane ring to open.

Thus, all of the calculations on the oxetane plus protonated oxetane [which we call (double oxetane)<sup>+</sup>] were carried out with our ab-initio MODPOT/VRDDO technique meshed in with the MRD-CI program.

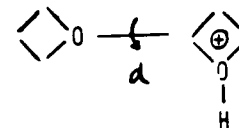
For the MRD-CI calculations on oxetane and protonated oxetanes themselves (and their ring opened species) (Figure 2),

DEFINITION OF  $\delta$ 

OXETANE



PROTONATED OXETANE

DEFINITION OF  $a$ 

we considered the localized orbitals in the  $C_4-O_1$  bond, the  $C_3-C_4$  bond, the  $C_2-C_4$  bond, the  $O_1-H^+$  bond, the lone pairs in  $O_1$  and the bonds connecting hydrogens to  $C_2$  and  $C_4$ .

We first ran a modest size CI calculation. We monitored the contributions of the various configurations to the wave function at each point. From these CI results we picked the most important reference configurations, generated all single and double excitations with respect to all the reference configurations, estimated by a perturbative procedure the energy contributions of each configuration, set a threshold (0.000035 a.u.), carried out the MRD-CI calculations, added back in the perturbative energy contributions of configurations not included explicitly in the MRD-CI, extrapolated to get  $E_{EXT}$  and then added the Davidson type correction to help account for size extensivity.

There were several significant results on the single ring compounds:

1. While for the closed ring oxetane the ground state SCF wave function contributed ~96% of the final MRD-CI wave function, for the ring opened oxetane ( $\delta = 19^\circ$ ) the ground state SCF wave function contributed only ~70% of the final MRD-CI wave function. Conversely, however, for the closed ring protonated oxetane, the SCF wave function contributed ~97% of the final MRD-CI wave function. Conversely, however, for the closed ring protonated oxetane the SCF wave function contributed ~97% of the final CI MRD-CI wave function. Analysis of the final wave function indicates

that in the case of the protonated oxetane both electrons remain with the oxygen atom when the  $C_4-O$  bond opens.

2. Inspection of the gross atomic populations (both SCF and MRD-CI) of protonated oxetane (Table I) indicates that there is not a positive charge on the protonated oxygen but a negative charge. This is due to the electronegativity of oxygen being larger than that of any of the other atoms. There are also varying degrees of negative charge on the carbon atoms in protonated oxetane since the carbons are more electronegative than the hydrogens. The positive charges reside on the hydrogen atoms. In oxetane itself the oxygen atom is somewhat less negatively charged than in protonated oxetane and the carbons have varying degrees of negative charge while there are positive charges on the hydrogen atoms. This charge redistribution has a profound influence on how one should consider the mechanism of the reaction between oxetanes and protonated oxetanes in the propagation step of cationic polymerization. In Table I the GAP's for the ring-opened oxetane and ring-opened protonated oxetane are presented also at the SCF and MRD-CI levels. The MRD-CI GAP on the oxygen of ring-opened oxetane is somewhat smaller than the GAP from the SCF result. This is due to the result that the ground state SCF wave function of ring-opened protonated oxetane only contributes ~70% to the final MRD-CI wave function.

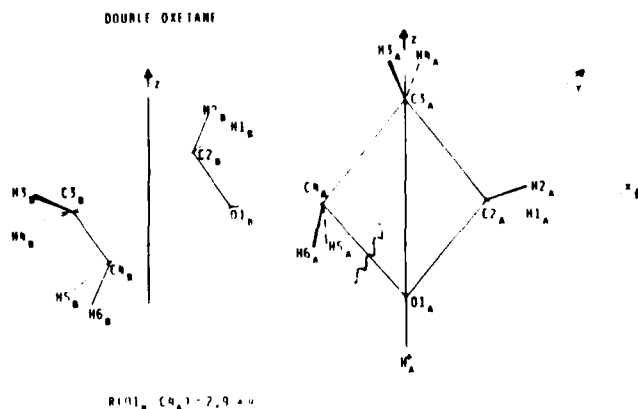
Table I

OXETANE AND PROTONATED OXETANE  
Ab-Initio MODPOT/VRDDO

Gross Atomic Populations - Valence Electrons Only

|     | <u>Oxetane</u>      |                   |               | <u>Protonated Oxetane</u> |                   |               |
|-----|---------------------|-------------------|---------------|---------------------------|-------------------|---------------|
|     | 0°                  | 19°               |               | 0°                        | 19°               |               |
|     | <u>fully closed</u> | <u>fully open</u> |               | <u>fully closed</u>       | <u>fully open</u> |               |
|     | <u>SCF</u>          | <u>SCF</u>        | <u>MRD-CI</u> | <u>SCF</u>                | <u>SCF</u>        | <u>MRD-CI</u> |
| O   | 6.36                | 6.27              | 6.17          | 6.46                      | 6.54              | 6.50          |
| C2  | 4.27                | 4.28              | 4.28          | 4.19                      | 4.22              | 4.21          |
| C3  | 4.45                | 4.45              | 4.45          | 4.45                      | 4.46              | 4.45          |
| C4  | 4.27                | 4.35              | 4.38          | 4.19                      | 4.03              | 4.04          |
| H1  | 0.78                | 0.78              | 0.78          | 0.70                      | 0.72              | 0.73          |
| H2  | 0.78                | 0.78              | 0.78          | 0.70                      | 0.72              | 0.73          |
| H3  | 0.77                | 0.77              | 0.77          | 0.71                      | 0.70              | 0.71          |
| H4  | 0.77                | 0.77              | 0.77          | 0.71                      | 0.70              | 0.71          |
| H5  | 0.78                | 0.77              | 0.80          | 0.70                      | 0.65              | 0.66          |
| H6  | 0.78                | 0.77              | 0.80          | 0.70                      | 0.65              | 0.66          |
| OH+ |                     |                   |               | 0.50                      | 0.59              | 0.60          |

We next carried out similar MRD-CI calculations for the cationic polymerization ring opening of protonated oxetanes by oxetane (Figure 3).



We have carried out calculations for a great many geometries for various paths of attack for the system oxetane plus protonated oxetane. We have varied the angle of opening of the protonated oxetane ring (ring 'A'), varied the internuclear distance between the rings and angle between the plane of the oxetane ring (ring 'B') and the plane of the protonated oxetane ring.

OXETANE PLUS PROTONATED OXETANE  
LOCALIZED ORBITALS USED EXPLICITLY IN MRD-CI CALCULATIONS

|                 |                 |          |
|-----------------|-----------------|----------|
| O <sub>1A</sub> | HO <sup>+</sup> | Occupied |
|-----------------|-----------------|----------|

|                 |                 |  |
|-----------------|-----------------|--|
| O <sub>1B</sub> | C <sub>4B</sub> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| O <sub>1B</sub> | C <sub>2B</sub> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| C <sub>4A</sub> | O <sub>1B</sub> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| C <sub>2A</sub> | O <sub>1A</sub> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| C <sub>4A</sub> | H <sub>6A</sub> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| C <sub>4A</sub> | O <sub>1A</sub> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| C <sub>4A</sub> | H <sub>5A</sub> |  |
|-----------------|-----------------|--|

|                   |             |  |
|-------------------|-------------|--|
| O <sub>1A</sub> , | (lone pair) |  |
|-------------------|-------------|--|

|                   |             |  |
|-------------------|-------------|--|
| O <sub>1B</sub> , | (lone pair) |  |
|-------------------|-------------|--|

---

|                 |                 |         |
|-----------------|-----------------|---------|
| C <sub>4A</sub> | H <sub>6A</sub> | Virtual |
|-----------------|-----------------|---------|

|                 |                 |  |
|-----------------|-----------------|--|
| O <sub>1B</sub> | C <sub>2B</sub> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| O <sub>1B</sub> | C <sub>4B</sub> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| O <sub>1A</sub> | HO <sup>+</sup> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| C <sub>4A</sub> | O <sub>1A</sub> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| C <sub>4A</sub> | O <sub>1B</sub> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| C <sub>4A</sub> | H <sub>5A</sub> |  |
|-----------------|-----------------|--|

|                 |                 |  |
|-----------------|-----------------|--|
| C <sub>2A</sub> | O <sub>1A</sub> |  |
|-----------------|-----------------|--|



GEOMETRY VARIATIONS FOR OXETANE (RING B)  
PLUS PROTONATED OXETANE (RING A)

- A 'A' ring  $\delta = 0^\circ$  (Closed Ring)
- B 'A' ring  $\delta = 5^\circ$
- E 'A' ring  $\delta = 19^\circ$  (Open Ring)
- F 'A' ring like propanol
- G 'A' ring propanol with H5A, H6A dihedral angles rotated by  $180^\circ$  to  $\pm 70^\circ$  (away from 'A' ring)
- H Same as 'G' but H5A, H6A ideally tetrahedral
- I Like 'E'  $\delta = 19^\circ$  H5A, H6A defined as in H

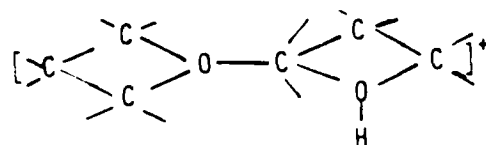
GEOMETRY - INTERNUCLEAR BETWEEN RINGS  
2.4, 2.9, 3.4, 3.9, 4.4, 4.9 a.u.

$\alpha$  value dihedral angle between rings  $90^\circ$ ,  $135^\circ$ ,  $180^\circ$  (coplanar)

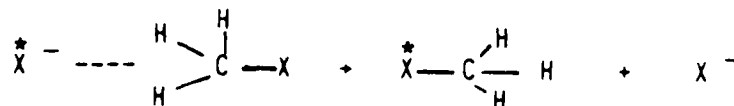
$\gamma$   $109.5^\circ$  tetrahedral around O1B  
 $132.94^\circ$  planar around O1B

$\theta$  angle of bonds around C4A

If oxetane approaches protonated oxetane as shown in Figure 3, our MRD-CI calculations indicate the interaction would be repulsive because of the interference of the 2 H atoms on C<sub>4A</sub>. Thus we have also carried out MRD-CI calculations pulling the positions of these two H atoms back from the approach of the attacking oxetane, as indicated below (Figure 4)

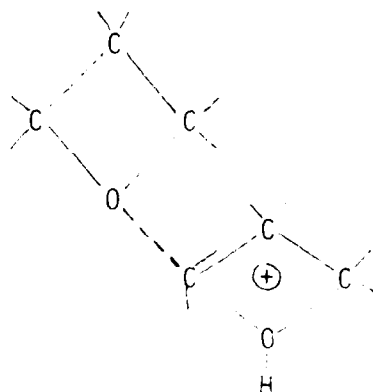


In discussions with several JHU organic chemists who are experts in the field of carbonium (carbocation) chemistry it was further suggested to us that a possible geometric pathway would be similar to an S<sub>N</sub>2 attack. An S<sub>N</sub>2 attack would have a similar pattern of five bonds (or incipient bonds) to a carbon in the intermediate. This would imply a general mechanism (Figure 5)

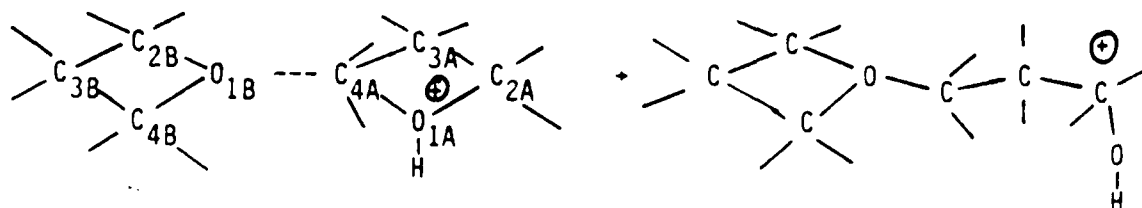


(where  $\text{X}^{\star -}$  is a closed shell species with an electron pair pointing toward the C) with an inversion (a Walden-type) inversion). In such a case an attack of  $\text{X}^{\star -}$  would be most favored if the attack of  $\text{X}^{\star -}$  were linear along the C - X bond direction. This mechanism applied to the oxetane plus protonated oxetane system with concomitant opening of the protonated oxetane ring would suggest that a possible favorable attack would be for the O<sub>1B</sub> of the oxetane ring to attack protonated oxetane along the line of the C<sub>4A</sub>-O<sub>1A</sub> bond. We are carrying out MRD-CI calculations for this mode of attack. Our

preliminary MRD-CI results appear favorable for forming a bond between  $O_{1B}$  and  $C_{4A}$  with concomitant opening of the  $C_{4A}-O_{1A}$  bond. (Figure 6)



Examination of the charge distribution of the oxetane plus protonated oxetane systems shows that in protonated oxetane there is not a positive charge on the O atom - but rather a negative charge. Also there are negative charges on the ring carbon atoms. The positive charges reside on the hydrogen atoms (both the H atoms on ring carbons and the H on the O). In the intermediate or product



there are still no positive charges on either of the oxygens or on the carbons (Table II). This is somewhat different than the charge distribution picture depicted to us by the experimentalists. This could have significant implications on visualizing the mechanism of the propagation step.

Table II

OXETANE PLUS PROTONATED OXETANE  
Ab-Initio MODOT/VRDDO

Gross Atomic Populations - Valence Electrons Only

$R_{OH} = 2.9$  bohr     $\delta = 19^\circ$      $\gamma = 132.94^\circ$     01A-C4A-01B Collinear

|     | <u>SCF</u> | <u>MRD-CI</u> |
|-----|------------|---------------|
| 01A | 6.57       | 6.53          |
| C2A | 4.24       | 4.26          |
| C3A | 4.45       | 4.45          |
| C4A | 4.19       | 4.19          |
| H1A | 0.75       | 0.75          |
| H2A | 0.75       | 0.75          |
| H3A | 0.75       | 0.75          |
| H4A | 0.75       | 0.75          |
| H5A | 0.71       | 0.72          |
| H6A | 0.71       | 0.72          |
| H0+ | 0.63       | 0.65          |
| 01B | 6.36       | 6.28          |
| C2B | 4.20       | 4.23          |
| C3B | 4.45       | 4.45          |
| C4B | 4.20       | 4.22          |
| H1B | 0.71       | 0.71          |
| H2B | 0.71       | 0.71          |
| H3B | 0.71       | 0.71          |
| H4B | 0.71       | 0.71          |
| H5B | 0.72       | 0.72          |
| H6B | 0.72       | 0.72          |

The total overlap populations (TOP's) of the oxetane plus protonated oxetane system for a particular path of attack (Table III) clearly indicate that for the system where the protonated oxetane ring ('A' ring) is open ( $\delta=19^\circ$ ) that the inter-ring TOP<sub>01B-C4A</sub> gets larger from an O<sub>1B</sub>-C<sub>4A</sub> inter-ring distance of 4.4 bohrs up until the energy minimum at 2.9 bohrs and then starts to get smaller. This indicates formation of an O<sub>1B</sub>-C<sub>4A</sub> bond.

Conversely, when the 'A' ring is closed ( $\delta=0^\circ$ ) the TOP<sub>01B-C4A</sub> gets more and more strongly negative (indicating repulsion) as the rings come closer. The intra-ring TOP<sub>01A-C4A</sub> of the closed protonated oxetane ring becomes less and less bonding as the oxetane approaches indicating that the protonated oxetane ring will tend to open upon attack by the oxetane. For many years we have found TOP's to be an excellent sensitive indicator of mechanisms of reactions.

Table III

## OXETANE PLUS PROTONATED OXETANE

## TOTAL OVERLAP POPULATIONS

## VALENCE ELECTRONS ONLY

| $R_{01B-C4A}$<br>(BOHRS) | 'A' Ring<br>$\delta = 0^\circ$<br>Fully Closed<br>TOP |                | 'A' Ring<br>$\delta = 19^\circ$<br>Fully Open<br>TOP |                |
|--------------------------|---|----------------|--|----------------|
|                          | <u>01B-C4A</u>  | <u>01A-C4A</u> | <u>01B-C4A</u>                                       | <u>01A-C4A</u> |
| 2.4                      | -0.49   | -0.05          | 0.39   | -0.03          |
| 2.9                      | -0.44   | 0.15           | 0.42   | -0.02          |
| 3.4                      | -0.28   | 0.28           | 0.37   | -0.01          |
| 3.9                      | -0.13   | 0.36           | 0.27   | -0.01          |
| 4.4                      | -0.06   | 0.39           | 0.17   | -0.00          |

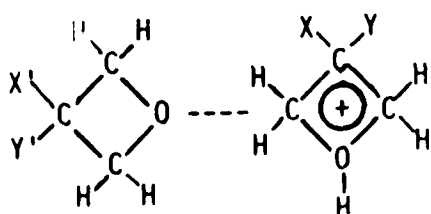
 $\alpha = 180^\circ$  $\gamma = 132.94^\circ$ 

01A-C4A-01B COLLINEAR

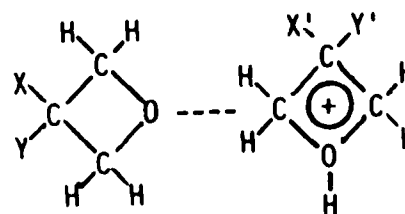
We have carried out calculations for a variety of different geometries as indicated above. The most favorable pathway we have found for oxetane attacking protonated oxetane is the one suggested to us by the JHU organic experimentalists, namely, that the  $O_{1B}$  (of oxetane) will prefer to attack linearly along the  $C_{4A}-O_{1A}$  bond (of protonated oxetane) with concomitant opening of the  $C_{4A}-O_{1A}$  bond.

For the MRD-CI calculation at each point, we monitor the contributions of the dominant and other possibly significant determinants to the MRD-CI wave functions.

Some representative results of the MRD-CI calculations are shown in Tables IV-XV. In these tables we list the number of configuration state functions generated and the number of these used in each step. the energies ( $E_{SCF}$ ,  $E_{CI}$ ,  $E_{EXT}$ , and  $E_{FULL}$ ), the  $\sum c^2$  (the sum of  $c^2$  of all of the reference configurations) and the  $c^2$  for each function contributing more than  $c^2 = 0.005$  to the final MRD-CI wave function. We are now initiating similar studies on substituted oxetanes and protonated oxetanes to understand their preferences for reacting with themselves or with other substituted species. This will give insight into copolymer propensities.



OR



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Table IV

## OXETANE PLUS PROTONATED OXETANE

Ab-Initio MODPOT/VRDDC MRD-CI

'A' ring  $\delta = 0^\circ$   $r = 2.4$  bohrs  $\alpha = 180^\circ$   $\gamma = 132.94^\circ$  01A-C4A-01B  
 fully closed collinear

|   |               | ENERGIES (a.u.)                                    |
|---|---------------|--|
| $E_{\text{SCF}}$                          |               | -70.751664   |
| $E_{\text{CI}}$                           |               | -70.945929<br>(891 csf's at 10 $\mu\text{H}$ )     |
| $E_{\text{EXT}}$                          |               | -70.953768<br>(30157 csf's generated)              |
| $E_{\text{FULL}}$                         |               | -70.957530   |
| $\sum c^2$                                |               | 0.9617   |
| GROUND STATE                              |               | 0.9070   |
| $(01\text{A}-\text{H}0+)^2$               | $\rightarrow$ | $(01\text{A}-\text{H}0+^*)^2$ 0.0065               |
| $(01\text{B}-\text{C}2\text{B})^2$        | $\rightarrow$ | $(01\text{B}-\text{C}2\text{B}^*)^2$ 0.0086        |
| $(\text{C}2\text{A}-01\text{A})^2$        | $\rightarrow$ | $(\text{C}2\text{A}-01\text{A}^*)^2$ 0.0097        |
| $(01\text{B}-\text{C}4\text{B})^2$        | $\rightarrow$ | $(01\text{B}-\text{C}4\text{B}^*)^2$ 0.0073        |
| $(\text{C}3\text{A}-\text{C}4\text{A})^2$ | $\rightarrow$ | $(\text{C}3\text{A}-\text{C}4\text{A}^*)^2$ 0.0064 |
| $(\text{C}4\text{A}-\text{H}5\text{A})^2$ | $\rightarrow$ | $(\text{C}4\text{A}-\text{H}5\text{A}^*)^2$ 0.0081 |
| $(\text{C}4\text{A}-\text{H}6\text{A})^2$ | $\rightarrow$ | $(\text{C}4\text{A}-\text{H}6\text{A}^*)^2$ 0.0081 |

Table V

## OXETANE PLUS PROTONATED OXETANE

Ab-Initio MODPOT/VRDDO MRD-CI

'A' ring  $\delta = 0^\circ$   $r = 2.9$  bohrs  $\alpha = 180^\circ$   $\gamma = 132.94^\circ$  01A-C4A-01B  
 fully closed collinear

|                             |   | ENERGIES (a.u.)                                |
|-----------------------------|---|--|
| $E_{\text{SCF}}$            |   | -71.077815                                     |
| $E_{\text{CI}}$             |   | -71.267822<br>(794 csf's at 10 $\mu\text{H}$ ) |
| $E_{\text{EXT}}$            |   | -71.274607<br>(33881 csf's generated)          |
| $E_{\text{FULL}}$           |   | -71.277755                                     |
| $\sum c^2$                  |   | 0.9639   |
| GROUND STATE                |   | 0.9074   |
| $(01\text{A-HO}^+)^2$       | ----> $(01\text{A-HO}^{+\star})^2$      | 0.0060   |
| $(\text{C}2\text{A-01A})^2$ | ----> $(\text{C}2\text{A-01A}^\star)^2$ | 0.0085   |
| $(01\text{B-C4B})^2$        | ----> $(01\text{B-C4B}^\star)^2$        | 0.0091   |
| $(\text{C}4\text{A-01A})^2$ | ----> $(\text{C}4\text{A-01A}^\star)^2$ | 0.0021   |
| $(01\text{B-C2B})^2$        | ----> $(01\text{B-C2B}^\star)^2$        | 0.0101   |
| $(\text{C}4\text{A-H6A})^2$ | ----> $(\text{C}4\text{A-H6A}^\star)^2$ | 0.0071   |
| $(\text{C}3\text{A-C4A})^2$ | ----> $(\text{C}3\text{A-C4A}^\star)^2$ | 0.0067   |
| $(\text{C}4\text{A-H5A})^2$ | ----> $(\text{C}4\text{A-H5A}^\star)^2$ | 0.0071   |

Table VI

## OXETANE PLUS PROTONATED OXETANE

Ab-Initio MODPOT/VRDDO MRD-CI

'A' ring  $\delta = 0^\circ$   $r = 3.4$  bohrs  $\alpha = 180^\circ$   $\gamma = 132.94^\circ$  01A-C4A-01B  
 fully closed collinear

|   |               | ENERGIES (a.u.)                                    |
|---|---------------|--|
| $E_{\text{SCF}}$                          |               | -71.230575   |
| $E_{\text{CI}}$                           |               | -71.415443<br>(692 csf's at 10 $\mu\text{H}$ )     |
| $E_{\text{EXT}}$                          |               | -71.421751<br>(33881 csf's generated)              |
| $E_{\text{FULL}}$                         |               | -71.424386   |
| $\sum c^2$                                |               | 0.9665   |
| GROUND STATE                              |               | 0.9073   |
| $(01\text{A}-\text{H}0+)^2$               | $\rightarrow$ | $(01\text{A}-\text{H}0+^*)^2$ 0.0057               |
| $(\text{C}3\text{A}-\text{C}4\text{A})^2$ | $\rightarrow$ | $(\text{C}3\text{A}-\text{C}4\text{A}^*)^2$ 0.0068 |
| $(\text{C}2\text{A}-01\text{A})^2$        | $\rightarrow$ | $(\text{C}2\text{A}-01\text{A}^*)^2$ 0.0078        |
| $(\text{C}4\text{A}-01\text{A})^2$        | $\rightarrow$ | $(\text{C}4\text{A}-01\text{A}^*)^2$ 0.0039        |
| $(01\text{B}-\text{C}4\text{B})^2$        | $\rightarrow$ | $(01\text{B}-\text{C}4\text{B}^*)^2$ 0.0105        |
| $(01\text{B}-\text{C}2\text{B})^2$        | $\rightarrow$ | $(01\text{B}-\text{C}2\text{B}^*)^2$ 0.0110        |
| $(\text{C}4\text{A}-\text{H}5\text{A})^2$ | $\rightarrow$ | $(\text{C}4\text{A}-\text{H}5\text{A}^*)^2$ 0.0063 |
| $(\text{C}4\text{A}-\text{H}6\text{A})^2$ | $\rightarrow$ | $(\text{C}4\text{A}-\text{H}6\text{A}^*)^2$ 0.0068 |

Table VII

## OXETANE PLUS PROTONATED OXETANE

Ab-Initio MODPOT/VRDDO MRD-CI

'A' ring  $\delta = 0^\circ$   $r = 4.4$  bohrs  $\alpha = 180^\circ$   $\gamma = 132.94^\circ$  01A-C4A-01B  
 fully closed collinear

|                       |  | ENERGIES (a.u.)                                |
|-----------------------|--|--|
| $E_{\text{SCF}}$      |  | -71.313176                                     |
| $E_{\text{CI}}$       |  | -71.492765<br>(545 csf's at 10 $\mu\text{H}$ ) |
| $E_{\text{EXT}}$      |  | -71.498149<br>(33881 csf's generated)          |
| $E_{\text{FULL}}$     |  | -71.500286                                     |
| $\sum c^2$            |  | 0.9696   |
| GROUND STATE          |  | 0.9072   |
| $(\text{O1A-HO}^+)^2$ | $\rightarrow (\text{O1A-HO}^{+\star})^2$ | 0.0054   |
| $(\text{C4A-H6A})^2$  | $\rightarrow (\text{C4A-H6A}^\star)^2$   | 0.0066   |
| $(\text{C4A-O1A})^2$  | $\rightarrow (\text{C4A-O1A}^\star)^2$   | 0.0059   |
| $(\text{C4A-H5A})^2$  | $\rightarrow (\text{C4A-H5A}^\star)^2$   | 0.0066   |
| $(\text{C3A-C4A})^2$  | $\rightarrow (\text{C3A-C4A}^\star)^2$   | 0.0070   |
| $(\text{O1B-C2B})^2$  | $\rightarrow (\text{O1B-C2B}^\star)^2$   | 0.0120   |
| $(\text{O1B-C4B})^2$  | $\rightarrow (\text{O1B-C4B}^\star)^2$   | 0.0119   |

Table VIII

## OXETANE PLUS PROTONATED OXETANE

Ab-Initio MODPOT/VRDDO MRD-CI

'A' ring  
fully open $\delta = 19^\circ$   $r = 2.4$  bohrs  $\alpha = 180^\circ$   $\gamma = 132.94^\circ$ 01A-C4A-01B  
collinear

|   |               | <u>ENERGIES (a.u.)</u>                             |
|---|---------------|--|
| $E_{\text{SCF}}$                          |               | -71.267994   |
| $E_{\text{CI}}$                           |               | -71.436155<br>(546 csf's at 10 $\mu\text{H}$ )     |
| $E_{\text{EXT}}$                          |               | -71.440836<br>(33881 csf's generated)              |
| $E_{\text{FULL}}$                         |               | -71.442487   |
| $\sum c^2$                                |               | 0.9742   |
| GROUND STATE                              |               | 0.9164   |
| $(01\text{A}-\text{H}0+)^2$               | $\rightarrow$ | $(01\text{A}-\text{H}0+^*)^2$ 0.0080               |
| $(01\text{B}-\text{C}4\text{B})^2$        | $\rightarrow$ | $(01\text{B}-\text{C}4\text{B}^*)^2$ 0.0069        |
| $(\text{C}3\text{A}-\text{C}4\text{A})^2$ | $\rightarrow$ | $(\text{C}3\text{A}-\text{C}4\text{A}^*)^2$ 0.0066 |
| $(01\text{B}-\text{C}4\text{A})^2$        | $\rightarrow$ | $(\text{C}4\text{A}-01\text{B}^*)^2$ 0.0028        |
| $(01\text{B}-\text{C}2\text{B})^2$        | $\rightarrow$ | $(01\text{B}-\text{C}2\text{B}^*)^2$ 0.0071        |
| $(\text{C}2\text{A}-01\text{A})^2$        | $\rightarrow$ | $(\text{C}2\text{A}-01\text{A}^*)^2$ 0.0125        |
| $(\text{C}4\text{A}-\text{H}6\text{A})^2$ | $\rightarrow$ | $(\text{C}4\text{A}-\text{H}6\text{A}^*)^2$ 0.0068 |
| $(\text{C}4\text{A}-\text{H}5\text{A})^2$ | $\rightarrow$ | $(\text{C}4\text{A}-\text{H}5\text{A}^*)^2$ 0.0069 |

Table IX

## OXETANE PLUS PROTONATED OXETANE

Ab-Initio MODPOT/VRDDO MRD-CI

'A' ring  
fully open $\delta = 19^\circ$   $r = 2.9$  bohrs  $\alpha = 180^\circ$   $\gamma = 132.94^\circ$ 01A-C4A-01B  
collinearENERGIES (a.u.) $E_{\text{SCF}}$ 

-71.342800

 $E_{\text{CI}}$ 

-71.515734

(520 csf's at 10  $\mu\text{H}$ ) $E_{\text{EXT}}$ 

-71.520481

(33881 csf's generated)

 $E_{\text{FULL}}$ 

-71.522302

 $\sum c^2$ 

0.9720

## GROUND STATE

0.9112

 $(01\text{A}-\text{H}0+)^2 \rightarrow (01\text{A}-\text{H}0+^*)^2$ 

0.0078

 $(\text{C}4\text{A}-\text{H}5\text{A})^2 \rightarrow (\text{C}4\text{A}-\text{H}5\text{A}^*)^2$ 

0.0067

 $(01\text{B}-\text{C}4\text{B})^2 \rightarrow (01\text{B}-\text{C}4\text{B}^*)^2$ 

0.0073

 $(01\text{B}-\text{C}2\text{B})^2 \rightarrow (01\text{B}-\text{C}2\text{B}^*)^2$ 

0.0074

 $(\text{C}2\text{A}-01\text{A})^2 \rightarrow (\text{C}2\text{A}-01\text{A}^*)^2$ 

0.0124

 $(01\text{B}-\text{C}4\text{A})^2 \rightarrow (\text{C}4\text{A}-01\text{B}^*)^2$ 

0.0058

 $(\text{C}3\text{A}-\text{C}4\text{A})^2 \rightarrow (\text{C}3\text{A}-\text{C}4\text{A}^*)^2$ 

0.0067

 $(\text{C}4\text{A}-\text{H}6\text{A})^2 \rightarrow (\text{C}4\text{A}-\text{H}6\text{A}^*)^2$ 

0.0067

Table X

## OXETANE PLUS PROTONATED OXETANE

Ab-Initio MODPOT/VRDDO MRD-CI

'A' ring  
fully open $\delta = 19^\circ$   $r = 3.4$  bohrs  $\alpha = 180^\circ$   $\gamma = 132.94^\circ$ 01A-C4A-01B  
collinearENERGIES (a.u.) $E_{\text{SCF}}$ 

-71.322213

 $E_{\text{CI}}$ 

-71.497370

(510 csf's at 10  $\mu\text{H}$ ) $E_{\text{EXT}}$ 

-71.501523

(33881 csf's generated)

 $E_{\text{FULL}}$ 

-71.503595

 $\sum c^2$ 

0.9689

## GROUND STATE

0.9058

 $(01A-HO+)^2 \rightarrow (01A-HO+^*)^2$ 

0.0077

 $(C2A-01A)^2 \rightarrow (C2A-01A^*)^2$ 

0.0122

 $(C4A-H5A)^2 \rightarrow (C4A-H5A^*)^2$ 

0.0066

 $(02B-C2B)^2 \rightarrow (02B-C2B^*)^2$ 

0.0079

 $(01B-C4B)^2 \rightarrow (01B-C4B^*)^2$ 

0.0078

 $(C4A-H6A)^2 \rightarrow (C4A-H6A^*)^2$ 

0.0066

 $(C3A-C4A)^2 \rightarrow (C3A-C4A^*)^2$ 

0.0066

 $(01B-C4A)^2 \rightarrow (C4A-01B^*)^2$ 

0.0077

Table XI

## OXETANE PLUS PROTONATED OXETANE

Ab-Initio MODPOT/VRDDO MRD-CI

'A' ring  
fully open $\delta = 19^\circ$   $r = 4.4$  bohrs  $\alpha = 180^\circ$   $\gamma = 132.94^\circ$ O1A-C4A-O1B  
collinear

|               |               | <u>ENERGIES (a.u.)</u>                   |
|---------------|---------------|--|
| $E_{SCF}$     |               | -71.250019                               |
| $E_{CI}$      |               | -71.419391<br>(470 csf's at 10 $\mu H$ ) |
| $E_{EXT}$     |               | -71.423061<br>(33881 csf's generated)    |
| $E_{FULL}$    |               | -71.425320                               |
| $\sum c^2$    |               | 0.9650                                   |
| GROUND STATE  |               | 0.9037                                   |
| $(O1B-C4B)^2$ | $\rightarrow$ | $(O1B-C4B^*)^2$ 0.0092                   |
| $(O1A-HO+)^2$ | $\rightarrow$ | $(O1A-HO+^*)^2$ 0.0075                   |
| $(C4A-H6A)^2$ | $\rightarrow$ | $(C4A-H6A^*)^2$ 0.0065                   |
| $(C4A-H5A)^2$ | $\rightarrow$ | $(C4A-H5A^*)^2$ 0.0065                   |
| $(C2A-O1A)^2$ | $\rightarrow$ | $(C2A-O1A^*)^2$ 0.0121                   |
| $(C3A-C4A)^2$ | $\rightarrow$ | $(C3A-C4A^*)^2$ 0.0064                   |
| $(O1B-C2B)^2$ | $\rightarrow$ | $(O1B-C2B^*)^2$ 0.0093                   |
| $(O1B-C4A)^2$ | $\rightarrow$ | $(C4A-O1B^*)^2$ 0.0036                   |



Table XII

## OXETANE PLUS PROTONATED OXETANE

Ab-Initio MODPOT/VRDDO MRD-CI

'A' ring  $\delta = 19^\circ$   $r = 2.4$  bohrs  $\alpha = 135^\circ$   $\gamma = 132.94^\circ$  01A-C4A-01B  
 fully open collinear

|               |               | <u>ENERGIES (a.u.)</u>                   |
|---------------|---------------|--|
| $E_{SCF}$     |               | -71.269251                               |
| $E_{CI}$      |               | -71.437514<br>(562 csf's at 10 $\mu H$ ) |
| $E_{EXT}$     |               | -71.441919<br>(33881 csf's generated)    |
| $E_{FULL}$    |               | -71.443578                               |
| $\sum c^2$    |               | 0.9741                                   |
| GROUND STATE  |               | 0.9164                                   |
| $(01A-HO+)^2$ | $\rightarrow$ | $(01A-HO+^*)^2$ 0.0080                   |
| $(C4A-01B)^2$ | $\rightarrow$ | $(C4A-01B^*)^2$ 0.0028                   |
| $(01B-C2B)^2$ | $\rightarrow$ | $(01B-C2B^*)^2$ 0.0071                   |
| $(01B-C4B)^2$ | $\rightarrow$ | $(01B-C4B^*)^2$ 0.0070                   |
| $(C4A-H5A)^2$ | $\rightarrow$ | $(C4A-H5A^*)^2$ 0.0067                   |
| $(C2A-01A)^2$ | $\rightarrow$ | $(C2A-01A^*)^2$ 0.0125                   |
| $(C3A-C4A)^2$ | $\rightarrow$ | $(C3A-C4A^*)^2$ 0.0068                   |
| $(C4A-H6A)^2$ | $\rightarrow$ | $(C4A-H6A^*)^2$ 0.0069                   |

## OXETANE PLUS PROTONATED OXETANE

Ab-Initio MODPOT/VRDDO MRD-CI

'A' ring  
fully open $\delta = 19^\circ$   $r = 2.9$  bohrs  $\alpha = 135^\circ$   $\gamma = 132.94^\circ$ O1A-C4A-O1B  
collinear

|               |               | ENERGIES (a.u.)                          |
|---------------|---------------|--|
| $E_{SCF}$     |               | -71.343003                               |
| $E_{CI}$      |               | -71.515998<br>(528 csf's at 10 $\mu H$ ) |
| $E_{EXT}$     |               | -71.515998<br>(33881 csf's generated)    |
| $E_{FULL}$    |               | -71.522023                               |
| $\sum c^2$    |               | 0.9721                                   |
| GROUND STATE  |               | 0.9112                                   |
| $(O1A-HO+)^2$ | $\rightarrow$ | $(O1A-HO+^*)^2$ 0.0078                   |
| $(C4A-H5A)^2$ | $\rightarrow$ | $(C4A-H5A^*)^2$ 0.0066                   |
| $(O1B-C4B)^2$ | $\rightarrow$ | $(O1B-C4B^*)^2$ 0.0073                   |
| $(O1B-C2B)^2$ | $\rightarrow$ | $(O1B-C2B^*)^2$ 0.0074                   |
| $(C2A-O1A)^2$ | $\rightarrow$ | $(C2A-O1A^*)^2$ 0.0124                   |
| $(C4A-H6A)^2$ | $\rightarrow$ | $(C4A-H6A^*)^2$ 0.0067                   |
| $(O1B-C4A)^2$ | $\rightarrow$ | $(C4A-O1B^*)^2$ 0.0058                   |
| $(C3A-C4A)^2$ | $\rightarrow$ | $(C3A-C4A^*)^2$ 0.0067                   |

Table XIV

## OXETANE PLUS PROTONATED OXETANE

Ab-Initio MODPOT/VRDDO MRD-CI

'A' ring  
fully open $\delta = 19^\circ$   $r = 4.4$  bohrs  $\alpha = 135^\circ$   $\gamma = 132.94^\circ$ 01A-C4A-01B  
collinear

|               |                       | ENERGIES (a.u.)                          |
|---------------|-----------------------|--|
| $E_{SCF}$     |                       | -71.249965                               |
| $E_{CI}$      |                       | -71.419232<br>(463 csf's at 10 $\mu H$ ) |
| $E_{EXT}$     |                       | -71.423010<br>(33881 csf's generated)    |
| $E_{FULL}$    |                       | -71.425265                               |
| $\sum c^2$    |                       | 0.9651                                   |
| GROUND STATE  |                       | 0.9038                                   |
| $(01B-C4B)^2$ | ----> $(01B-C4B^*)^2$ | 0.0093                                   |
| $(01A-HO+)^2$ | ----> $(01A-HO+^*)^2$ | 0.0075                                   |
| $(C4A-H5A)^2$ | ----> $(C4A-H5A^*)^2$ | 0.0065                                   |
| $(C2A-01A)^2$ | ----> $(C2A-01A^*)^2$ | 0.0121                                   |
| $(C3A-C4A)^2$ | ----> $(C3A-C4A^*)^2$ | 0.0064                                   |
| $(01B-C2B)^2$ | ----> $(01B-C2B^*)^2$ | 0.0093                                   |
| $(C4A-H6A)^2$ | ----> $(C4A-H6A^*)^2$ | 0.0066                                   |
| $(01B-C4A)^2$ | ----> $(C4A-01B^*)^2$ | 0.0036                                   |

Table XV

OXETANE PLUS PROTONATED OXETANE  
MRD-CI Ab-Initio MODPOT/VRDDO  
Energies (a.u.) and Binding Energies (a.u.)

|            | Oxetane<br>$\delta = 0^\circ$<br>fully closed | Protonated<br>Oxetane<br>$\delta = 0^\circ$<br>fully closed | Protonated<br>Oxetane<br>$\delta = 19^\circ$<br>fully open | Double<br>Oxetane <sup>+</sup><br>* | Binding<br>Energy<br>$[DOX^+ - (OX + OX^+)]$<br>$\delta = 0^\circ$ | Binding<br>Energy<br>$\delta = 19^\circ$ |
|------------|---|---|--|-------------------------------------|--|--|
| $E_{SCF}$  | -35.499691                                    | -35.809020  | -35.701723   | -71.342800                          | -0.034039  | -0.141385                                |
| $E_{CI}$   | -35.621127                                    | -35.932007  | -35.809049   | -71.515734                          | +0.037400  | -0.085558                                |
| $E_{EXT}$  | -35.622857                                    | -35.934264  | -35.810758   | -71.520481                          | +0.036640  | -0.086866                                |
| $E_{FULL}$ | -35.623814                                    | -35.935307  | -35.811764   | -71.522302                          | +0.036819  | -0.086724                                |

Double Oxetane<sup>+</sup>  $[DOX^+]$  = Oxetane plus Protonated Oxetane

OX = Oxetane

OX<sup>+</sup> = Protonated Oxetane

\* = ('A' ring fully open,  $r_{O1B-C4A} = 2.9$  bohr,  $\alpha = 180^\circ$ ,  $\gamma = 132.94$ ;  $O1A-C4A-O1B$  collinear)

### III. $^{17}\text{O}$ NMR Spectra of Oxetanes

The  $^{17}\text{O}$  NMR spectra of several oxetanes were examined experimentally by Walter S. Koski to see if they could be used to calibrate our computed electrostatic molecular potential contour (EMPC) maps for the basicity of oxetane and its derivatives. The results for oxetane and BAMO show that  $^{17}\text{O}$  NMR chemical shifts cannot be used directly to make such calibrations. The reasons for this is that two opposing effects contribute to the resultant chemical shift. One is a diamagnetic effect, related to the electron density on the O nucleus, and a second is a paramagnetic effect, due to the presence of low lying excited states. It is difficult to unscramble these two contributions and get a direct measure of the electron population on the oxygen atom. However as we point out below, a detailed study of these NMR shifts coupled with other experimental chemico-physical/physicochemical measurements plus theoretical interpretation would make valuable contributions to our knowledge of oxetane and its energetic derivatives.

Certain properties such as basicity and electron density around the oxetane play an important role in cationic polymerization reactions involving oxetane and its energetic derivatives. Ab-initio quantum chemical calculations and electrostatic molecular potential contour (EMPC) maps enable one to get a rank measure of the propensity of oxetane and its derivatives to undergo initiation of polymerization. It would be highly desirable to determine experimentally a property such as electron density on the oxygen atoms of some of these compounds. Such measurements would be of great value as calibration points for the quantum chemically computed electrostatic molecular potential contour maps to put them on a more quantitative absolute scale. To this end we have made a preliminary examination of using  $^{17}\text{O}$  NMR chemical shifts to see if they reflect the electron density around the oxygen in oxetane and 3,3-bis(azidomethyl)oxetane (BAMO). Neat samples of liquids were carefully dried and sealed in 10 mm. tubes using  $\text{D}_2\text{O}$  as an external standard. The measurements were made on a Varian 400 XL spectrometer.

Intuitively it would be expected on the basis of inductive effects that the oxygen in oxetane would have a higher electron density and thus would be more shielded than the oxygen in BAMO. This is confirmed by the calculated electrostatic molecular potential contour (EMPC) maps and the calculated volumes enclosed within corresponding isopotential EMPC contours.  $^{17}\text{O}$  NMR chemical shifts in oxetane and BAMO indicate that the opposite is true for the shielding.  $^{17}\text{O}$  in oxetane falls 10 ppm lower than  $^{17}\text{O}$  in  $\text{D}_2\text{O}$  whereas  $^{17}\text{O}$  in BAMO lies 31.4 ppm on the high field side of  $\text{D}_2\text{O}$ , indicating that the O in BAMO is more shielded than the O in unsubstituted oxetane. The reason for this is that there are two competing effects contributing to the position of the nuclear magnetic resonance. The first is a diamagnetic shielding effect caused by the motion of electrons around the nucleus in question (related to the electron density on the O nucleus) and the second is a paramagnetic term (due to the presence of low lying excited states). The sign of the paramagnetic term is opposite to that of the diamagnetic

effect. The effects of these two terms are difficult to disentangle quantitatively. This phenomenon is exemplified by the studies of Beraldin et al.<sup>1</sup> on the relationships between NMR shifts and atomic charge on  $^{17}\text{O}$  in ethers. Their results show that in a series of aliphatic ethers, any gain in electronic charge at the oxygen atom is accompanied by a downfield  $^{17}\text{O}$  NMR shift. This is at variance with the frequently held view that any increase in local electron population should increase shielding of the nucleus in question and hence produce an upfield shift.

Similarly Iwamura et al.<sup>2</sup> studied the NMR  $^{17}\text{O}$  shifts in twenty-one oxiranes and found it necessary to bring in diamagnetic, paramagnetic and other effects to rationalize the observed results.

However, a detailed  $^{17}\text{C}$  and  $^{13}\text{C}$  NMR study of substituted oxetanes coupled with other chemicophysical/physicochemical measurements would give us a great deal of insight into the electronic properties of the series of energetic oxetane derivatives of interest to this ONR program.

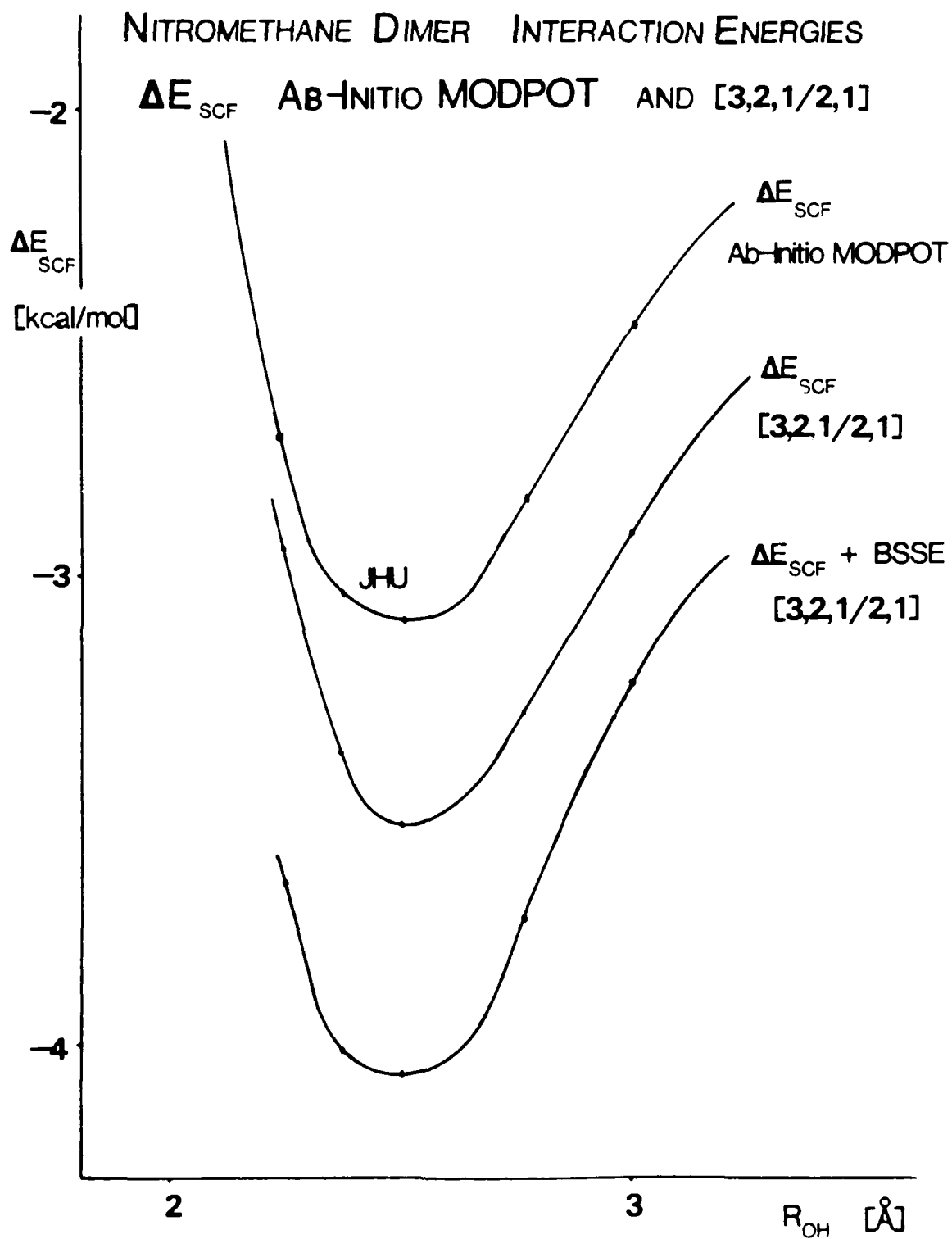
1. M. T. Beraldin, E. Vauthier and S. Flizar, *Can. J. Chem.* 60, 106 (1982).
2. H. Iwamura, T. Sugawara, Y. Klawada, K. Tori, R. Muneyuki and R. Noyori, *Tetrahedron Letters*, 36, 3449 (1979).

#### IV. Ab-initio Atom-Class - Atom-Class Potential Functions and Independent Confirmations of the Validity of Our Ab-Initio MODPOT/VRDDO Energy Partitioned Method For Intermolecular Interactions.

Over the past several years we had developed and implemented methods for deriving ab-initio atom-class - atom-class potential functions from ab-initio energy partitioned SCF calculations plus dispersion energy.<sup>1</sup> The SCF calculations were done with our INTER-MOLASYS program. That program is completely general for Gaussian integrals either all-electron or with the MODPOT option of using ab-initio effective core model potentials. Our earlier research on intermolecular interactions calculated with our ab-initio MODPOT well balanced minimal basis set showed these basis sets have comparatively little BSSE (basis set superposition error) compared to all-electron calculations. The reason for this is that while even fairly large all-electron basis sets may describe the inner shells reasonably well, the small deficiency in the inner shell wave function is very heavily energy weighted and can contribute significant energy to the BSSE. On the other hand, our ab-initio MODPOT minimal all-electron basis set had been optimized to reproduce molecular charge distributions resulting from larger well balanced basis sets. Then our ab-initio MODPOT parameter was optimized to reproduce the valence electron molecular orbital energies and charge distributions of that all-electron well balanced minimal basis set. The optimization of the MODPOT basis set for reproducing molecular charge distributions of larger basis sets makes that basis set more reliable than other customarily used minimal atomic basis sets for calculating intermolecular interaction energies of compounds, such as nitrocompounds and other compounds with electronegative groups (such as azido, nitro, and nitramino) with large intramolecular charge redistribution, since the multipole part of the electrostatic component  $E_{EL,MTP}^{(1)}$  of intermolecular interaction energies is customarily the most significant term.

As a minor effort of this past year's ONR research (but with significant favorable implications for our ONR research), we recently had the opportunity to validate the reliability both of the SCF intermolecular interaction calculations using the ab-initio MODPOT basis set and of the semi-theoretical expressions we had been using for dispersion energy by comparing our results on the nitromethane dimer with those of recent larger basis set [4,3,1/2,1] all-electron calculations on the nitromethane dimer<sup>2</sup>, [SCF, SCF/SQ-MBPT(4), SCF/dispersion energy  $E_{disp}^{(200)}$ ]. Our ab-initio MODPOT SCF minimum energy occurred at the same intermolecular distance as the SCF minimum of the all-electron larger basis set. Our ab-initio MODPOT SCF interaction energy corrected for BSSE (-3.10 kcal/mol at 2.5 Å) was only 0.4 kcal above the SCF interaction energy of the larger basis set (-3.57 kcal/mol corrected for BSSE at the minimum 2.5 Å). (Figure 7)

Figure 7

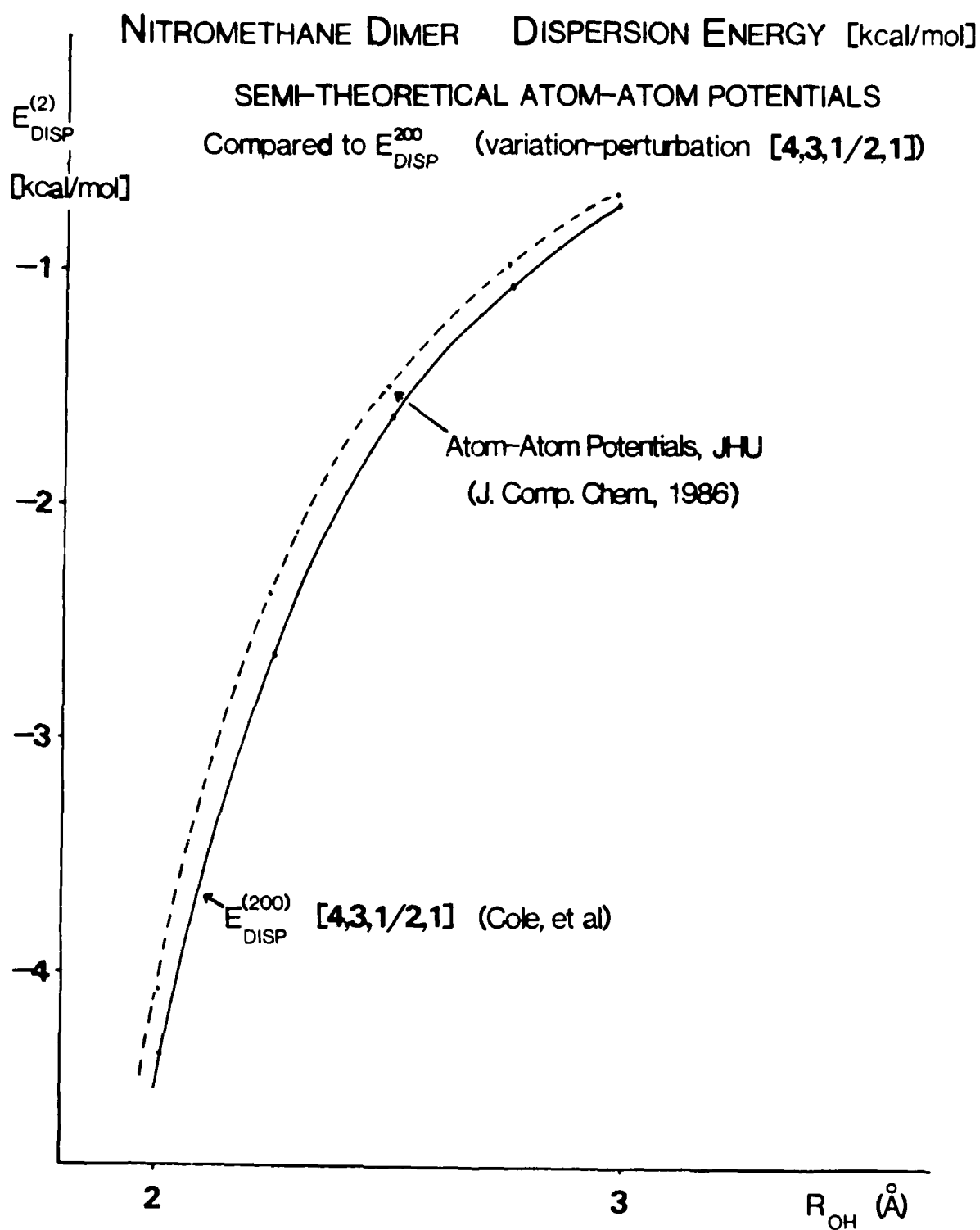




Furthermore, we also carried out the ab-initio MODPOT energy-partitioned SCF calculations on the nitromethane dimer to ascertain the magnitudes of the various contributions to the interaction energy. We then calculated the value of the  $E_{EL,MTP}^{(1)}$  using the multipoles calculated for nitromethane at the SCF level [ $E_{EL,MTP}^{(1)SCF}$  with the all-electron larger basis set used in reference 2]. This was done to enable us to see the genesis of the small differences in  $E_{SCF}$  at the SCF minimum between our ab-initio MODPOT SCF calculations and the larger all-electron SCF calculations. Our previous experience had indicated that the major difference in intermolecular interaction energies between our ab-initio minimal MODPOT SCF calculations and larger basis set calculations lay in a small difference in  $E_{EL,MTP}^{(1)}$  calculated with the different basis sets. Our present results on the nitromethane dimer confirmed this hypothesis. At the SCF minimum (2.50 Å) the  $E_{EL,MTP}^{(1)SCF}$  we calculated for the nitromethane dimer with the ab-initio MODPOT basis set was -4.58 kcal/mole; the  $E_{EL,MTP}^{(1)SCF}$  we calculated with the larger all-electron [4,3,1/2,1] basis set was -5.09 kcal/mole. This difference, at the SCF minimum (2.50 Å) in  $E_{EL,MTP}^{(1)SCF}$  (0.51 kcal/mole) is very close to the difference in SCF interaction energies (0.44 kcal/mole) at the SCF minimum. This correction is certainly expected to be valid for  $R > R_{eq}$ . For the intermolecular separation of 2.5 Å, 2.7 Å, and 3.0 Å the correction for the difference in  $E_{EL,MTP}^{(1)SCF}$  (calculated explicitly at each point) brings our total calculated interaction energies within 0.1 kcal of the  $\Delta E_{SCF}$  values for the larger basis set. Our ab-initio MODPOT SCF method (which, depending on the molecules involved, is an order to orders of magnitude more rapid than all-electron larger basis set SCF calculations) could, therefore be used to calculate intermolecular interaction energies to locate the SCF minimum. Our results further suggest that it appears feasible to correct for the small differences in the absolute intermolecular interaction energies between the ab-initio MODPOT SCF results and those of all-electron larger basis set SCF calculations by the difference in the  $E_{EL,MTP}^{(1)}$  calculations with the different basis sets.

In addition, the semi-theoretical method we have been using to estimate dispersion energies proved to give values very close to  $E_{DISP}^{(200)}$  (variation-perturbation) calculated by Cole et al. using a larger all-electron basis set. (Figure 8)

Figure 8



We also explored another aspect. Cole, et al. had calculated the  $E_{\text{SDQ-MBPT}(4)}$  interaction energy of the nitromethane dimer as the difference between  $E_{\text{SDQ-MBPT}(4)}(\text{nitromethane dimer}) - 2E_{\text{SDQ-MBPT}(4)}(\text{nitromethane monomer})$ . This  $E_{\text{SDQ-MBPT}}$  intermolecular interaction energy includes both intermolecular correlation energy and the correlation contribution to the intermolecular interaction energy from correlated intramolecular (monomer) wave functions. We calculated  $E_{\text{EL,MTP}}^{(1)\text{SDQ-MBPT}(4)}$  for the nitromethane dimer using the correlated multipoles from nitromethane monomer which we computed by carrying out correlated SDQ-MBPT(4) calculations for nitromethane monomer with the larger all-electron basis set of Cole et al. excluding excitations from inner shells.

$\Delta E_{\text{INTRA,EL}}^{\text{CORR}}$  (correlation correction to intermolecular interaction electrostatic term from multipoles due to use of correlated intramolecular monomer wave functions)

$$\begin{aligned}
 &= E_{\text{EL,MTP}}^{(1)\text{SDQ-MBPT}(4)} (\text{Cole, et al. basis set}) - E_{\text{EL,MTP}}^{(1)\text{SCF}} (\text{Cole, et al. basis set}) \\
 &= -4.087 \text{ kcal/mole} - (-5.086 \text{ kcal/mole}) \\
 &= 0.999 \text{ kcal/mole (at nitromethane dimer equilibrium geometry)} \\
 &= \Delta E_{\text{INTRA}}^{\text{CORR}} (\text{correlation contribution to intermolecular interaction energy from intermolecular correlation contributions due to correlated monomer wave functions}) \\
 &= E_{\text{INTER}}^{\text{SDQ-MBPT}(4)} \{ \text{intermolecular correlation effects plus the correlation contribution to intermolecular interaction energy from correlated monomer wave functions (at the SDQ-MBPT(4) level)} \} \\
 &\quad - E_{\text{DISP}}^{(2)} \{ \text{intermolecular correlation effects (dispersion)} \} \\
 &= -0.76 \text{ kcal/mole (at nitromethane equilibrium dimer) [Cole, et al.]} \\
 &\quad - 1.65 \text{ kcal/mole (at nitromethane equilibrium dimer) [Cole, et al.]} \\
 &= 0.89 \text{ kcal/mole.}
 \end{aligned}$$

This correction should be valid for  $R > R_{\text{eq}}$ .

These results suggest how one might use  $E_{\text{EL,MTP}}^{(1)\text{SDQ-MBPT}(4)}$  and  $E_{\text{EL,MTP}}^{(1)\text{SCF}}$  results to separate intermolecular correlation contributions to intermolecular interaction energies and correlation contributions to

intermolecular interactions energies which arise from use of correlated monomer wave functions.

1. "Crystal Structure Studies Using Ab-Initio Potential Functions From Partitioned Ab-Initio MODPOT/VRDDO SCF Energy Calculations. I.  $N_2$  and  $CO_2$  Test Cases. II. Nitromethane," W. Sokalski, S. Roszak, P. C. Hariharan, W. S. Koski, Joyce J. Kaufman, A. H. Lowrey, and R. S. Miller. Int. J. Quantum Chem., S17, 375-391 (1983).
2. S. J. Cole, K. Szalewicz, G. D. Purvis, III and R. J. Bartlett, J. Chem. Phys. 84, 6883 (1986)

## V. Geometry Optimizations at the MC-SCF/CI Level

We explored a number of the features of the GAMESS program which has the capability of optimizing geometries by a derivative method at the MC-SCF/CI and CASSCF levels as well as at the SCF level. As prototype problems we have successfully optimized the geometries of oxetane, protonated oxetane and nitromethane at the RHF SCF level and we have successfully optimized the geometry of nitromethane at the MC-SCF level. (Nitromethane was an excellent test case since Dr. Kaufman had previously used the GAMESS program for MC-SCF type calculations on the  $>\text{C} - \text{NO}_2$  decomposition pathway of nitromethane.) We will be carrying out further studies to investigate the effect of basis set size, balance, polarization functions, etc. We will also be exploring and using more of the new options in the GAMESS program for our studies on the energetic oxetanes.

It will, of course, always still be necessary first to sample through space by carrying out the quantum chemical calculations explicitly at various geometries to find the locations of the various local maxima and minima since geometry optimizations by derivative methods lead only to the local minimum in the region selected as the starting geometry. This is where our own ab-initio MODPOT/VRDDO/MERGE methods are so useful.

We are also initiating derivative calculations for geometry optimizations of other substituted oxetanes and substituted protonated oxetane we have investigated as a prelude to MRD-CI calculations for their interactions. For some of the larger substituted oxetanes we are having to enlarge or modify the techniques in GAMESS.

We are also investigating carrying out ab-initio derivative calculations using the GAMESS program for the most probable conformations of the product of the propagation step in the cationic polymerization of oxetane by protonated oxetane. This is a more difficult problem. In accord with our previous experience because of multiple maxima and minima one must start with a geometry in the region of each minimum. Also if one is too far from a minimum, the derivative method may not converge or may converge to a saddle point. We use our ab-initio MODPOT/VRDDO/MERGE SCF techniques to identify reasonable starting conformations

## VI. POLY-CRYST

Commensurate with the ONR priorities expressed to us by our ONR Contract Monitor to devote our major attention to the problem of the cationic polymerization of oxetanes, we only devoted very minimal effort to further development and testing of the POLY-CRYST program (for ab-initio calculations of crystals and polymers).

For efficiency we initiated changes in the way the integrals are picked up. We also ran a few test calculations. The strategy for testing is to calculate the energy of the isolated molecule and the cluster of molecules in the unit reference cell with our ab-initio molecular (MOLASYS) or intermolecular programs (INTER-MOLASYS). Then we repeat the calculation on the unit reference cell with POLY-CRYST with  $\vec{k} = 0$ . The energy of the cluster of molecules in the unit reference cell (by INTER-MOLASYS) and that of the unit reference cell by POLY-CRYST must agree. We then run the POLY-CRYST calculations for a number of cells.

The POLY-CRYST program has great potential for understanding properties of energetic molecular crystals. We hope that in the future ONR priorities will be such that we can devote more attention to this research area.

## VII. Lectures Presented and Publications on This ONR Research

Presentations given and or scheduled and papers published and/or submitted during the fiscal year

## A. Presentations Given Dr. Joyce J. Kaufman

1. Already presented (\* denotes invited lecture)
  - a. National and International Meetings
    - \* "Ab-Initio MRD-CI Calculations of the  $>\text{C} - \text{NO}_2$  Decomposition Pathway of Nitrobenzene," Sanibel International Symposia on Quantum Chemistry, Solid State Theory, Many-Body Phenomena and Computational Quantum Chemistry, Marineland, Florida, March 1986
    - \* "Ab-Initio Multireference Double Excitation Configuration Interaction Calculations Based on Localized Orbitals for Molecular Decompositions and Reactions for Large Systems," Sanibel International Symposia on Quantum Chemistry, Solid State Theory, Many-Body Phenomena and Computational Quantum Chemistry, Marineland, Florida, March 1986.
    - "More New Desirable Computational Strategies for Ab-Initio Calculations on Large Molecules, Clusters, Solids and Crystals," Sanibel International Symposia Snowbel Satellite on Interface Between Electronic Structures and Dynamics, Snowbird, Utah, April 1986.
    - \* "Ab-Initio MRD-CI Calculations on the  $>\text{C} - \text{NO}_2$  Decomposition Pathway of Nitrobenzene," plenary lecture presented at the Symposium on Computational and Mathematical Chemistry, Can. Inst. Chem. National Meeting, Saskatoon, Canada, June 1986.
    - \* "Ab-Initio Potentials for Crystals and Ab-Initio Crystal Orbitals," special invited lecture presented at the International Symposium on Molecules in Physics, Chemistry and Biology, dedicated to Professor R. Daudel, Paris, France, June 1986.
    - \* "Ab-Initio Localized Orbital MRD-CI Calculations on the Mechanism of Cationic Polymerization of Oxetane By Protonated Oxetane," IUPAC 5th International Symposium on Ring-Opening Polymerization, Blois, France, June 1986.
    - \* "Ab-Initio Multireference Double Excitation Configuration Interaction Calculations Based on Localized Orbitals for Molecular Decompositions and Reactions for Large Systems,," American Chemical Society National Meeting, Anaheim, Calif., September 1986.

b. Other Research Institutions

- \* "Ab-Initio Calculations on Large Molecules, Crystals and Solids Using Desirable Computational Strategies," Sandia Laboratories, Albuquerque, New Mexico, May 1986.
- \* "Ab-Initio Calculations on Large Molecules, Crystals and Solids Using Desirable Computational Strategies," Los Alamos National Laboratory, New Mexico, May 1986.

2. To be Presented

a. National and International Meetings

- \* "Ab-Initio MRD-CI Calculations for the Prediction of Cationic Polymerization of Oxetanes Based on Localized Orbitals," Sanibel International Symposia on Atomic, Molecular and Solid State Theory, Many-Body Phenomena and Computational Methods, Marineland, Florida, March 1987.
- \* "Comparison of Ab-Initio MODPOT and Ab-Initio Energy Partitioned Potential Functions for Nitromethane Dimer Against Large Basis Set Calculations," Sanibel International Symposia on Atomic, Molecular and Solid State Theory, Many-Body Phenomena and Computational Methods, Marineland, Florida, March 1987.
- \* "Ab-Initio Calculations on Large Molecules and Solids Using Desirable Computational Strategies," VIIIth International Conference on Computers in Chemical Research and Education, Beijing, China, June 1987.

b. Other Research Organizations

- \* "Ab-Initio Quantum Chemical Calculations on Large Molecular Systems and Crystals", Maryland Section American Chemical Society, February 1987.

c. At Department of Defense Meetings

- \* "Ab-Initio Multireference Determinant Configuration Interaction Calculations for the Propagation Step in Cationic Polymerization of Oxetanes," ONR Workshop on Polymeric Energetic Materials Synthesis, Great Oak, Maryland, October 1986.
- \* "Ab-Initio MRD-CI (Multireference Double Excitation Configuration Interaction) and Ab-Initio Intermolecular Interaction Calculations on Energetic Nitrocompounds," ONR Workshop on Crystalline Energetic Materials Synthesis, Great Oak, Maryland, November 1986.



## B. Papers Published on This ONR Research, October 1985-September 1986

## 1. Already Published

- a. "Ab-Initio Multireference Determinant Configuration Interaction (MRD-CI) and CASSCF Calculations on Energetic Compounds," Joyce J. Kaufman, P. C. Hariharan, S. Roszak, C. Chabalowski, M. van Hemert, M. Hotokka and R. J. Buenker. In CHEMICAL REACTION DYNAMICS, NATO Advanced Study Institute, Editors P. M. Rentzepis and C. Capellos, D. Reidel Publishers, Dordrecht, Netherlands, 1986, pp. 289-310.
- b. "Crystal Structures of Energetic Compounds: Ab-Initio Potential Functions and Ab-Initio Crystal Orbitals," Joyce J. Kaufman, P. C. Hariharan, S. Roszak, J. M. Blaisdell and A. H. Lowrey, and R. S. Miller. In CHEMICAL REACTION DYNAMICS, NATO Advanced Study Institute, Editors, P. M. Rentzepis and C. Capellos, D. Reidel Publishers, Dordrecht, Netherlands, 1986, pp. 311-326.
- c. "POLY-CRYST - A Program for Ab-Initio Crystal Orbitals and Polymer Orbitals," J. J. Blaisdell, W. A. Sokalski, P. C. Hariharan and Joyce J. Kaufman. J. Non-Crystalline Solids, 75, 319-326 (1985).
- d. "Procedure Supplementing SCF Interaction Energies By Dispersion Term Evaluated in Dimer Basis Within Variation Perturbation Approach," S. Roszak, W. A. Sokalski, P. C. Hariharan and Joyce J. Kaufman. Theo. Chim. Acta., 70, 81-88 (1986).

## 2. Accepted For Publication and In Press

- a. "Ab-Initio Localized Orbital MRD-CI Calculations on the Mechanism of Cationic Polymerization of Oxetane By Protonated Oxetane," Joyce J. Kaufman, P. C. Hariharan, S. Roszak and M. Hotokka. An invited lecture presented at the IUPAC 5th International Symposium on Ring-Opening Polymerization, Blois, France, June 1986. In Press, Makromolekular Chemie, special Symposium Issue.
- b. "Ab-Initio MRD-CI Calculations on the  $>\text{C}-\text{NO}_2$  Decomposition Pathway of Nitrobenzene," Joyce J. Kaufman, P. C. Hariharan, S. Roszak and M. van Hemert. An invited plenary lecture presented at the Symposium on Computational and Mathematical Chemistry, Can. Inst. Chem. National Meeting, Saskatoon, Canada, June 1986. In press, J. Comp. Chem., Symposium Issue.
- c. "Symposium Note: More New Desirable Computational Strategies for Ab-Initio Calculations on Large Molecules,

Clusters, Solids and Crystals," Joyce J. Kaufman. In press, Int. J. Quantum Chem., Symposium Issue.

- d. "Nonempirical Atom-Atom Potentials for Main Components of Intermolecular Interaction Energy," W. A. Sokalski, A. H. Lowrey, S. Roszak, V. Lewchenko, J. M. Blaisdell, P. C. Hariharan and Joyce J. Kaufman. In press, J. Comp. Chem.

## VIII. Project Personnel

Joyce J. Kaufman, Ph.D.

Principal Investigator

P. C. Hariharan, Ph.D.

Research Scientist

Overall responsibility for implementing new program developments and conversion to CRAY computers.

Quantum chemical calculations on energetic polymers, MRD-CI, GAMESS and POLY-CRYST calculations

Philip B. Keegstra, Ph.D.

Post Doctoral

MRD-CI calculations on cationic polymerization of oxetanes, test calculations on POLY-CRYST.

Robert J. Buenker, Ph.D.

Visiting Collaborator (March-April 1986)

Initiated expansion of MRD-CI program to include more reference configurations, more roots and a post MRD-CI population analysis for NRL CRAY XMP-12 (COS).

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Marc van Hemert, Ph.D.

Visiting Collaborator (June-July 1986)

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S. Roszak Ph.D.

Visiting Associate Research Scientist (July 1985 - January 1986)

Test MRD-CI calculations to validate use of localized orbitals  
MRD-CI calculations for cationic polymerization - opening the oxetane ring (neutral and protonated).

W. A. Sokalski, Ph.D.

Visiting Associate Research Scientist (August-September 1986)

Program developments for correlated wave functions. Test of our MODPOT and additional methods against large basis set calculations for nitromethane dimer.

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